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(54) Title: HYDROCARBON CONVERSION PROCESS

(57) Abstract

An improved method for converting methane to higher hydrocarbon products by contacting a gas comprising methane with a contact agent at a selected temperature, the agent comprising a reducible metal oxide, a support of oxides of silicon or alkaline earth metal, and an alkali metal.

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HYDROCARBON CONVERSION PROCESS

BACKGROUND OF THE INVENTION

Field of the Invention

This invention relates to the synthesis of hydrocarbons from a methane source. A particular application of this invention is a method for converting natural gas to more readily transportable material using a methane conversion catalyst formed using a reducible metal oxide; a support of at least one member of a group consisting of oxides of silicon, oxides of alkaline earth metals, and mixed oxides thereof; and an alkali metal.

Description of the Pertinent Art

A major source of methane is natural gas. Other sources of methane have been considered for fuel supply (e.g., the methane present in coal deposits or formed during mining operations). Relatively small amounts of methane are also produced in various petroleum processes.

The composition of natural gas at the wellhead varies, but the major hydrocarbon present is methane. For example, the methane content of natural gas may vary within the range of about 40 to about 95 volume percent. Other constituents of natural gas include ethane, propane, butane, pentane (and heavier hydrocarbons), hydrogen sulfide, carbon dioxide, helium, and nitrogen.

Natural gas is classified as dry or wet, depending upon the amount of condensable hydrocarbons contained in it. Condensable hydrocarbons generally comprise C_3+ hydrocarbons, although some ethane may be included. Gas conditioning is required to alter the composition of wellhead gas; processing facilities usually being located in or near the production fields. Conventional processing of wellhead natural gas yields processed natural gas containing at least a major amount of methane.

Large-scale use of natural gas often requires a sophisticated and extensive pipeline system. Liquefaction has also been employed as a transportation means, but processes for liquefying, transporting and revaporizing natural gas are complex, energy intensive and require extensive safety precautions. Transport of natural gas has been a continuing problem in the exploitation of natural gas resources. It would be extremely valuable to be able to convert methane (e.g., natural gas) to more readily transportable products. Moreover, direct conversion to olefins such as ethylene or propylene would be extremely valuable to the chemical industry.

Recently, it has been discovered that methane may be converted to higher hydrocarbons by a process which comprises contacting methane with an oxidative synthesizing agent at synthesizing conditions (e.g., at a temperature selected within the range of about 500° to about 1000°C.). An oxidative synthesizing agent is a composition having as a principal component at least one oxide of at least one metal, which composition produces higher C_2+ hydrocarbon products, water and a composition comprising a reduced metal oxide when contacted with methane at synthesizing conditions. Reducible oxides of several metals have been identified which are capable of converting methane to higher hydrocarbons. In particular, oxides of manganese, tin, indium, germanium, lead, antimony and bismuth are most useful.

The reaction products of such processes are mainly ethylene, ethane, other light hydrocarbons, carbon oxides, coke and water. It would be beneficial to these oxidative synthesis processes to reduce the production of carbon oxides and coke.

Accordingly, an object of this invention is to provide an improved process for converting methane to higher hydrocarbons. A further object of this invention is an improved oxidative synthesizing agent--one capable of converting methane with reduced byproduct selectivities.

Other aspects, objects and the several advantages of this invention will become apparent to those skilled in the art upon reading this Specification and the appended claims.

SUMMARY OF THE INVENTION

An improved hydrocarbon conversion process has been discovered which comprises contacting hydrocarbons, preferably a gas comprising methane, with a contact agent at conditions to convert the hydrocarbons, preferably at a temperature selected within the range of about 500° to about 1000°C., which agent comprises:

(a) at least one reducible oxide of at least one metal, which oxide is reduced and produces higher hydrocarbon products and water when contacted with methane at the selected temperature;

(b) an alkali metal; and

(c) a support comprising at least one member of a group consisting of oxides of silicon, oxides of alkaline earth metals, and mixed oxides of silicon and at least one alkaline earth metal.

DETAILED DESCRIPTION OF THE INVENTION

The contact agent of this invention is a composition comprising at least one reducible oxide of at least one metal and a support. The reducible oxide produces higher hydrocarbon products, water and a reduced metal oxide when contacted with methane at a temperature selected within the range of about 500° to about 1000°C. The term "reducible" is used to identify those oxides of metals which are reduced by contacting methane at synthesizing conditions. The term "oxide(s) of metal(s)" includes: (1) one or more metal oxides (i.e., compounds described by the general formula M_xO_y wherein M is a metal, O is oxygen, and the subscripts x and y designate the relative atomic proportions of metal and oxide in the composition); and/or (2) one or more oxygen-containing metal compounds; provided that such oxides and compounds have the capability of performing to produce higher hydrocarbon products as set forth herein.

The preferred contact agents comprise reducible oxides of metals selected from a group consisting of manganese, tin, indium, germanium, antimony, lead, bismuth, and mixtures thereof. The particularly preferred contact agents comprise reducible oxides of manganese and mixtures of reducible oxides of manganese with other oxidative synthesizing agents.

In the preferred embodiment, in addition to manganese, other reducible oxides of metals may be included in the compositions of this invention. These other reducible oxides of metals include tin, indium, germanium, antimony, lead, bismuth, praseodymium, terbium, cerium, iron, and ruthenium. However, in certain embodiments of this invention, the compositions are characterized by the substantial absence of a catalytically effective amount of iron to distinguish known oxidative dehydrogenation catalysts based on the use of manganese ferrites.

One class of preferred compositions is characterized by the substantial absence of catalytically effective amounts of nickel and the noble metals (e.g., rhodium, palladium, silver, osmium, iridium, platinum, and gold) and compounds thereof to minimize the deleterious catalytic effects of such metals and compounds thereof. For example, at the conditions (e.g., temperatures) under which the present compositions are used, these metals tend to promote coke formation and oxides of these metals tend to promote the formation of combustion products (CO_x), rather than the desired hydrocarbons. The term "catalytically effective" is used to identify that quantity of nickel, the noble metals, and compounds thereof which, when present, substantially changes the distribution of products obtained when employing the compositions of this invention.

The support comprises oxides of silicon, oxides of alkaline earth metals, and mixtures thereof. Preferably, the support comprises at least two oxides. Preferably, at least one of the oxides is an alkaline earth oxide and the second oxide is silica. More preferably, the first oxide comprises magnesia.

The preferred mole ratio of the first oxide to the silica is 1:1 or greater, and more preferably is in the range of about 30:1 to about 5:1. Particularly good results are obtained when this ratio is about 5:1.

Examples of specific embodiments within this broad class are described below.

$MnA_aSi_bO_x$

Another class of compositions within the scope of this invention comprises manganese-containing oxides, at least one alkali metal or compound thereof, and at least one oxide of silicon, said composition satisfying the formula:

$$MnA_aSi_bO_x$$

wherein A is at least one alkali metal, a is within the range of about 0.01 to about 10, b is within the range of about 0.5 to about 90, and x is the number of oxygen atoms required by the valence states of the other elements, said composition being substantially free of catalytically effective iron. Preferably, b is within the range of about 0.9 to about 17.4, more preferably about 2 to about 15. The silicon component may be provided as silica. However, use of other materials is also within the scope of this invention. For example, the defined composition may be derived from braunite, a native manganese silicate having the formula $MnSiO_3 \cdot Mn_2O_3$.

$MnA_aMg_bO_x$

Another class of compositions within the scope of this invention comprises manganese-containing oxides, at least one alkali metal component, and at least one oxide of magnesium, said composition satisfying the formula:

$$MnA_aMg_bO_x$$

wherein A is at least one alkali metal, a is within the range of about 0.01 to about 10, b is within the range of about 1.4 to about 130, and x is the number of oxygen atoms required by the valence states of the other elements. Preferably, b is within the range of about 3 to about 80, more preferably about 5 to about 12. The magnesium component is preferably provided as magnesia.

$MnA_aB_bO_x$

Another class of compositions within the scope of this invention comprises manganese-containing oxides, at least one alkali metal or compound thereof, and at least one member of a group consisting of oxides of calcium, strontium, and barium, said composition satisfying the formula:

$$MnA_aB_bO_x$$

wherein A is at least one alkali metal, B is at least one member of a group consisting of calcium, strontium, and barium, a is within the range of about 0.01 to about 10, b is within the range of about 0.1 to about 100, and x is the number of oxygen atoms required by the valence states of the other elements. Preferably, b is within the range of about 1 to about 7.

Compositions described by the formula $MnA_aCa_bO_x$ are presently preferred. In this case, b is preferably within the range of about 0.4 to about 100, more preferably within the range of about 4 to about 20.

Oxides of calcium, strontium, and barium are preferably provided as CaO, SrO, and BaO, respectively.

$MnA_aB_bSi_cO_x$

Another class of compositions within the scope of this invention comprises manganese-containing oxides, at least one alkali metal or compound thereof, and mixed oxides of silicon and alkaline earth metals, said composition satisfying the formula:

$$MnA_aB_bSi_cO_x$$

wherein A is at least one alkali metal, B is at least one alkaline earth metal, a is within the range of about 0.1 to about 10, b is within the range of about 0.1 to about 90, c is within the range of about 1 to about 90, the sum of b plus c is greater than about 1, and x is the number of oxygen atoms required to satisfy the valence states of the other elements. When B is magnesium, b is preferably within the range of about 0.6 to about 10. When B is calcium, b is preferably within the range of about 0.4 to about 10. When B is barium, b is preferably within the range of about 0.1 to about 5.

While the relative amounts of alkaline earth metals and silicon in the composition are not believed to be narrowly critical, preferred SiO_2-MgO components have been identified. One component consists of silica-magnesia wherein the ratio c:b is within the range of about 2-3:1. Another component consists of magnesia-silica wherein the ratio b:c is within the range of about 5-30:1.

The composition may be prepared from silica and alkaline earth oxides such as MgO, CaO, SrO, and BaO. However, other sources of mixed oxides may also be employed (e.g., $MgSiO_4$, $MgSiO_3$, Mg_2SiO_4, $CaMg(SiO_3)_2$, and $Ca_2BaSi_3O_9$).

The term "hydroxylated magnesia" means a magnesia derived from magnesium hydroxide or a magnesium-containing component contacted with a hydroxyl-containing component. The hydroxylated magnesia is preferably derived from magnesium hydroxide (e.g., magnesia produced from sea water). One such suitable magnesia is commercially available from CRI Industries as MgO-700.

Alternatively, the hydroxylated magnesia may be derived from sources other than magnesium hydroxide such as a magnesium-containing component contacted with a hydroxyl-containing material (e.g., one or more compounds including hydroxyl groups). Such hydroxyl-containing material includes sodium hydroxide, potassium hydroxide, lithium hydroxide, slake lime, calcium hydroxide, and hydroxides of barium. One method of producing the present hydroxylated magnesia comprises contacting a magnesium-containing component with (a) water for an extended period or (b) boiling water. Any suitable magnesium-containing component may be employed to produce hydroxylated magnesia. Examples include magnesia, magnesium chloride, and magnesium salts.

One important feature of the present invention is the precalcination of the hydroxylated magnesia support prior to the addition of the at least one metal. The hydroxylated magnesia is calcined prior to the addition of the at least one metal at an elevated temperature in an oxygen-containing gas. The particular precalcining temperature will vary, but preferably it will be between about 300° and about 1200°C.

The support is preferably prepared in powdered form, more preferably having a particle size ranging from about 20 to about 200 microns, and still more preferably about 100 microns. The support is dried to the extent that upon subsequent sintering the particles do not steam or explode. Preferably, the particles have a water content of less than about 1.0 weight percent water.

Preferably, the support is sintered to an elevated temperature (i.e., heated to a high temperature without melting the support) by exposure for a short time to a temperature high enough to cause at least partial fusion of the surface of the particles. This exposure can occur before or after the addition of the metal which forms at least one reducible oxide (e.g., derived from sodium or lithium permanganate, or mixtures of manganese and sodium, or lithium salts). The elevated (sintering) temperature varies with the composition of the material being sintered. In one preferred embodiment, the elevated temperature is equal to about 0.33 of the normal melting temperature of the material of the support.

Exposure to the high temperature may be accomplished by allowing the particles to briefly contact a flame or a hot surface. Alternatively, a laser or other electromagnetic radiation source with a limited depth of surface penetration of the support may be used. The degree of surface sintering can be controlled by the temperature of the flame or of the hot surface, by the intensity of the light, or by the length of time of exposure.

The particles should be removed from the heat source quickly so that the effect of the sintering is confined to the depth desired. Removal from the flame or hot surface can be accomplished by several means--by transporting the particles out of the region of the hot substance, by cooling the hot substance with another material, by contacting the particles with a heat sink to remove the heat absorbed from the hot substance, or by combinations of these and other methods. When a laser is used, its light can be diverted or adsorbed. Removal of heat by radiation or conduction is preferred.

The addition of steam or an inert gas (such as nitrogen) or a reactive gas (such as hydrogen chloride) is preferred to control the sintering process.

Preferred sintering temperatures for the support material are in the range of about 1690° to about 5070°F. for magnesia and about 1040° to about 3110°F. for silica. Sintering of the support may take place in a period of time in the range of about 0.5 minute to about 15 minutes or more, preferably in a period of time in the range of about 1 minute to about 10 minutes.

The method of the present invention preferably provides support compositions exhibiting a surface area ranging from about 30 to about 90 square meters per gram.

Preferably, the catalyst composition of this invention comprises manganese, the oxide of which is reducible, at least one alkali metal or compound thereof, and a support comprising at least one member of a group consisting of oxides of silicon, oxides of alkaline earth metals, and mixed oxides of silicon and at least one alkaline earth metal. In general, the preferred compositions contain more than about 50 weight percent of the support, more preferably they contain more than about 60 weight percent of the support. Stated in another way, manganese is preferably present in an amount within the range of about 1 to about 40 weight percent based on the combined weight of the manganese and the support, more preferably within the range of about 5 to about 30 weight percent. When the composition is prepared from alkaline earth oxides, this manganese loading is more preferably within the range of about 10 to about 20 weight percent. The atomic ratio of alkali metal to manganese is preferably within the range of about 0.01:1 to about 10:1.

Other additives may also be incorporated into the composition of this invention. For example, addition of a phosphorus component has been found to enhance the stability of the composition. When used, phosphorus may be present up to an amount providing a phosphorus-to-manganese ratio of about 2:1. If phosphorus is employed, it is desirable to provide it during catalyst preparation in the form of phosphates of alkali metals (e.g., orthophosphates, metaphosphates, and pyrophosphates). Pyrophosphates are preferred. Sodium pyrophosphate is particularly preferred. Phosphorus can be provided in other forms though. Examples include orthophosphoric acid, ammonium phosphates, and ammonium hydrogenphosphates.

Further examples of other components which may be present in the compositions of this invention include halogen and chalcogen components. Such components may be added either during preparation of the catalyst or during use.

The preferred contact agent of this invention contains, in addition to the foregoing elements, at least one alkali metal. Sodium and/or compounds thereof are a particularly preferred alkali metal component. Except as noted elsewhere herein, the atomic ratio in which these materials are combined to form the contact agent is not narrowly critical. However, the preferred atomic ratio of the reducible oxide component (expressed as the metal, e.g., Mn) to the alkali metal component (expressed as the metal, e.g., Na) is within the range of about 0.1:1 to about 100:1, more preferably within the range of about 0.3:1 to about 10:1. The preferred mole ratio of silica or alumina to alkali metal is about 50:1 to about 1:1, and more preferably about 0.5:1 to about 10:1. Most preferably, the ratio is about 1:1 to about 3:1.

The alkali metal component may be added to the support before or during precipitation, coprecipitation, or impregnation of the reducible oxide and the support.

The support or agent may be contacted with a suitable alkali metal component which should not interfere with the support function, the reducible oxide function, or the process for combining the support with the reducible oxide. Preferably, the alkali metal component is a basic composition of the alkali metal. More preferably, the alkali metal component is selected from a group consisting of sodium hydroxide, sodium acetate, lithium hydroxide, lithium acetate, and mixtures thereof.

The contact agent can be prepared by any suitable method. Conventional methods such as precipitation, coprecipitation, impregnation, granulation, and spray drying can be used.

One suitable method of preparation of the contact agent includes the preparation of an aqueous slurry of magnesia and silica gel and mixing the slurry with a solution of reducible oxides.

In a second suitable method, a support is prepared and dried, then impregnated with the suitable metal compounds which include acetates, acetylacetonates, oxides, carbides, carbonates, hydroxides, formates, oxalates, nitrates, phosphates, sulfates, sulfides, tartrates, fluorides, chlorides, bromides or iodides of the metals.

After the mixing of the slurry with the solution or the impregnation, the resulting composite is dried in an oven to remove solvent and the dried solid is prepared for use by calcining at elevated temperatures in an oxygen-containing gas (e.g., air) prior to use in the process of this invention. Particular calcination temperatures will vary, depending upon the particular metal compound or compounds employed. Preferably, the air temperature is selected within the range of about 300° to about 1200°C.

In addition to methane, the preferred feedstock employed in the method of this invention may contain other hydrocarbon or non-hydrocarbon components, although the methane content should typically be within the range of about 40 to about 100 volume percent, preferably about 80 to about 100 volume percent, more preferably about 90 to about 100 volume percent.

Operating temperatures for contacting the methane with the contact agent are preferably selected within the range of about 500° to about 1000°C.; the particular temperature selected depending upon the particular reducible metal oxide(s) employed in the contact agent. For example, reducible oxides of certain metals may require operating temperatures below the upper part of the recited range to minimize sublimation or volatilization of the metals (or compounds thereof) during methane contact. Examples include reducible oxides of indium, germanium and bismuth (operating temperatures will preferably not exceed about 850°C.).

Operating pressures for the methane contacting step are not critical to the presently claimed invention. However, both general system pressure and partial pressure of methane have been found to affect overall results. Preferred operating pressures are within the range of about 1 to about 30 atmospheres.

Contacting methane and a reducible metal oxide to form higher hydrocarbons from methane also produces reduced metal oxides and water. The exact nature of the reduced metal oxides is unknown, and so is referred to herein as "reduced metal oxides". Regeneration of a reducible metal oxide is readily accomplished by contacting such reduced materials with oxygen (e.g., an oxygen-containing gas such as air) at elevated temperatures, preferably at a temperature selected within the range of about 300° to about 1200°C.; the particular temperature selected depending on the metal(s) included in the contact agent.

In carrying out the present process, a single reactor apparatus containing a fixed bed of solids may be used with intermittent or pulsed flow of a first gas comprising methane followed by intermittent or pulsed flow of a second gas comprising oxygen (e.g., oxygen, oxygen diluted with an inert gas, or air, preferably air). The methane contacting step and the oxygen contacting step may also be performed in physically separate zones with solids recirculating between the two zones.

Thus, a suitable method for synthesizing hydrocarbons from a methane source comprises: (a) contacting a gas comprising methane and particles comprising a contact agent to form higher hydrocarbon products, water and reduced metal oxides; (b) removing particles comprising reduced metal oxides from the first zone and contacting the reduced particles in a second zone with an oxygen-containing gas to form particles comprising a contact agent; and (c) returning the particles produced in the second zone to the first zone. The steps are preferably repeated at least periodically, and more preferably the steps are continuous. In the more preferred embodiment, solids are continuously circulated between at least one methane contact zone and at least one oxygen contact zone.

Particles comprising a reducible metal oxide which are contacted with methane may be maintained as fluidized, ebullating, or entrained beds of solids. Preferably, methane is contacted with a fluidized bed of solids.

Similarly, particles comprising reduced metal oxides which are contacted with oxygen may be maintained as fluidized, ebullating, or entrained beds of solids. Preferably, oxygen is contacted with a fluidized bed of solids.

In the more preferred embodiment of the present invention, methane feedstock and particles comprising a contact agent are continuously introduced into a methane contact zone maintained at synthesizing conditions. Synthesizing conditions include the temperatures and pressures described above. Gaseous reaction products from the methane contact zone (separated from entrained solids) are further processed (e.g., passed through a fractionating system wherein the desired hydrocarbon products are separated from unconverted methane and combustion products). Unconverted methane may be recovered and recycled to the methane contact zone.

Particles comprising reduced metal oxides are contacted with oxygen in an oxygen contact zone for a time sufficient to oxidize at least a portion of the reduced metal oxides to produce a reducible metal oxide and to remove (i.e., combust) at least a portion of any carbonaceous deposit which may form on the particles in the methane contact zone. The conditions of the oxygen contact zone will preferably include a temperature selected within the range of about 300° to about 1200°C., pressures of up to about 30 atmospheres, and average particle contact time within the range of about 1 minute to about 120 minutes. Sufficient oxygen is preferably provided to oxidize all reduced metal oxides to produce a reducible metal oxide and to completely combust any carbonaceous deposit material deposited on the particles. At least a portion of the particles comprising the contact agent which are produced in the oxygen contact zone are returned to the methane contact zone.

Another more specific application for the compositions of this invention is the dehydrogenation of dehydrogenatable hydrocarbons. The process comprises contacting a gas comprising a dehydrogenatable hydrocarbon with a composition of this invention to produce dehydrogenated hydrocarbon products, water, and a composition comprising a reduced metal oxide. Dehydrogenatable hydrocarbons include a wide variety of hydrocarbons (e.g., C_2+ alkanes, cycloalkanes, olefins, alkylaromatics, etc.). The dehydrogenated product depends in part on the feedstock selected. For example, alkanes may be dehydrogenated to form olefins, diolefins, alkynes, etc., and olefins may be dehydrogenated to form diolefins, alkynes, etc. One preferred class of feedstock comprises C_2-C_4 alkanes. One preferred process embodiment comprises oxidative dehydrogenation of C_2-C_5 alkanes to form the corresponding mono-olefins.

Operating temperatures for such a process are generally within the range of about 500° to about 1000°C. Operating pressures are not narrowly critical. In general, the process is conducted within the parameters of the oxidative dehydrogenation art, but uses a novel catalyst.

The rate of solids withdrawal from the methane contact zone is desirably balanced with the rate of solids passing from the oxygen contact zone to the methane contact zone so as to maintain a substantially constant inventory of particles in the methane contact zone, thereby enabling steady-state operation of the synthesizing system.

The present invention is further illustrated by reference to the following Examples.

EXAMPLES

Methane contact runs were made at about atmospheric pressure in quartz tube reactors (12 mm. inside diameter) partially packed with 10 ml. of contact solids. The reactors were brought up to temperature under a flow of heated nitrogen which was switched to methane at the start of the run. Unless otherwise indicated, all methane contact runs described in the Examples had a duration of two minutes. At the end of each methane contact run, the reactor was flushed with nitrogen and the solids were regenerated under a flow of heated air (usually at 800°C. for 30 minutes). The reactor was then again flushed with nitrogen and the cycle repeated. Most of the results reported below are based on the cumulative samples collected after the contact solids were "equilibrated" (i.e., after the aberrant characteristics of the fresh contact solids had dissipated). This allows more meaningful comparison between the contact solids within the scope of the present invention and other contact solids. Three to six cycles of methane contact and regeneration are generally sufficient to equilibrate the contact solids.

Space velocities are reported as gas hourly space velocities ($hr.^{-1}$) (GHSV) and were 600 GHSV, except where indicated otherwise.

Example I

27.6 grams of $NaMnO_4$-$3H_2O$ (Pfaltz and Bauer SO-5560) were dissolved in 400 ml. of water. 138 grams of magnesia (Fisher MgO, heavy, U.S.P.) were calcined for 16 hours at 800°C. The sodium permanganate solution and the calcined magnesia were slurried for 1 hour at 150°F. The product was dried for 2 hours at 230°F., crushed and then screened through a 60-mesh sieve. The powder was then calcined for 16 hours at 800°C.

Example II

27.6 grams of $NaMnO_4$-$3H_2O$ (Pfaltz and Bauer SO-5560) were dissolved in 300 ml. of water. 122 grams of magnesia (Fisher MgO, heavy, U.S.P.) were calcined for 16 hours at 550°C. The sodium permanganate solution, 100 grams of colloidal silica (Nalco 2326), and the calcined magnesia were slurried for 1 hour at 150°F. The product was dried for 2 hours at 230°F., crushed and then screened through a 60-mesh sieve. The powder was then calcined for 16 hours at 800°C.

Example III

27.6 grams of $NaMnO_4$-$3H_2O$ (Pfaltz and Bauer SO-5560) were dissolved in 525 ml. of water. The solution and 144 grams of magnesia (Catalyst Resources, Inc. MgO-700 precursor (without addition of silica)) were slurried for 1 hour at 150°F. The solid material was dried for 2 hours at 230°F., crushed and then screened through a 60-mesh sieve. The powder was then calcined for 16 hours at 800°C.

Example IV

27.6 grams of $NaMnO_4$-$3H_2O$ (Pfaltz and Bauer SO-5560) were dissolved in 300 ml. of water. The solution, 128 grams of magnesia (Catalyst Resources, Inc. MgO-700 precursor (without addition of silica)) and 100 grams of colloidal silica (Nalco 2326) were slurried for 1 hour at 150°F. The solid material was dried for 2 hours at 230°F., crushed and then screened through a 60-mesh sieve. The powder was then calcined for 16 hours at 800°C.

Example V

534 grams of $NaMnO_4$-$3H_2O$ (Pfaltz and Bauer SO-5560) were dissolved in 1500 ml. of water and diluted up to 1900 ml. 2620 grams of magnesia (Basic Chemical Co. Magox 95) were calcined for 16 hours at 550°C. The calcined magnesia was impregnated with the sodium permanganate solution. The product was dried for 2 hours at 230°F., crushed and then screened through a 60-mesh sieve. The powder was then calcined for 16 hours at 800°C.

Example VI

27.6 grams of $NaMnO_4$-$3H_2O$ (Pfaltz and Bauer SO-5560) were dissolved in 100 ml. of water. The sodium permanganate solution, 100 grams of colloidal silica

2326) and 307 grams of magnesia (Basic Chemical Co. Magox 95 precursor, mud) were slurried for 1 hour at 150°F. The product was dried for 2 hours at 230°F., crushed and then screened through a 60-mesh sieve. The powder was then calcined for 16 hours at 800°C.

Example VII

27.6 grams of $NaMnO_4$-$3H_2O$ (Pfaltz and Bauer SO-5560) were dissolved in 400 ml. of water. 138 grams of magnesia (Malinckrodt MgO, U.S.P.) were calcined for 16 hours at 800°C. The sodium permanganate solution and the calcined magnesia were slurried for 1 hour at 150°F. The product was dried for 2 hours at 230°F., crushed and then screened through a 60-mesh sieve. The powder was then calcined for 16 hours at 800°C.

Example VIII

27.6 grams of $NaMnO_4$-$3H_2O$ (Pfaltz and Bauer SO-5560) were dissolved in 300 ml. of water. 122 grams of magnesia (Malinckrodt MgO, U.S.P.) were calcined for 16 hours at 550°C. The sodium permanganate solution, 100 grams of colloidal silica (Nalco 2326) and the calcined magnesia were slurried for 1 hour at 150°F. The product was dried for 2 hours at 230°F., crushed and then screened through a 60-mesh sieve. The powder was then calcined for 16 hours at 800°C.

Table 1

Ex. No.	Test No.	Na	Mn	Mg	Si	% Conv.	% Selec.	% C_2 Yield
		Atomic Ratio vs. Na						
I	5511-09	1	1	24.0	--	14.2	81.8	11.6
II	5508-20	1	1	21.0	1.8	20.5	65.6	13.4
III	5523-06	1	1	24.0	--	14.2	11.2	1.6
IV	5526-09	1	1	21.0	1.8	20.7	58.9	12.2
V	5504-19	1	1	24.0	--	13.0	52.6	6.8
VI	5524-01	1	1	21.0	1.8	19.0	48.7	9.3
VII	5515-01	1	1	24.0	--	14.3	82.5	11.8
VIII	5501-08	1	1	21.0	1.8	15.3	59.1	9.0

The silica/magnesia support associated with the reducible oxide is shown to be more selective than its counterpart with the silica/magnesia support.

Example IX

470 grams of $NaMnO_4$-$3H_2O$ (Pfaltz and Bauer SO-5560) were dissolved in 1000 ml. of water and diluted to 2617 ml. 2380 grams of magnesia (Catalyst Resources, Inc. MgO-700 tabletted magnesia) were crushed and calcined for 16 hours at 550°C. The calcined magnesia was impregnated with the sodium permanganate solution. The product was dried for 2 hours at 230°F., and then calcined for 16 hours at 800°C.

Example X

27.6 grams of $NaMnO_4$-$3H_2O$ (Pfaltz and Bauer SO-5560) were dissolved in 100 ml. of water and diluted to 130 ml. 138 grams of magnesia (Fisher MgO, heavy, U.S.P.) were calcined for 16 hours at 550°C. The calcined magnesia was impregnated with the sodium permanganate solution. The product was dried for 2 hours at 230°F. and then calcined for 16 hours at 800°C.

Example XI

27.6 grams of $NaMnO_4$-$3H_2O$ (Pfaltz and Bauer SO-5560) were dissolved in 100 ml. of water and diluted to

130 ml. 138 grams of magnesia (Martin-Marietta 500 G30) were calcined for 16 hours at 550°C. The sodium permanganate solution was impregnated onto the calcined magnesia. The product was dried for 2 hours at 230°F. and then calcined for 16 hours at 800°C.

Example XII

534 grams of $NaMnO_4$-$3H_2O$ (Pfaltz and Bauer SO-5560) were dissolved in 1500 ml. of water and diluted to 1900 ml. 2620 grams of magnesia (Basic Chemical Co. Magox 95) were calcined for 16 hours at 550°C. The calcined magnesia was impregnated with the sodium permanganate solution. The product was dried for 2 hours at 230°F., crushed and then screened through a 60-mesh sieve. The powder was then calcined for 16 hours at 800°C.

Results reported below in Table 2 are based on the analysis of cumulative samples collected during the third two-minute methane contact run for each contact agent. Run conditions were 800°C.

Table 2

Example No.	Test No.	Cycle	% Conv.	% Selec.	% C_2 Yield
IX	5511-08	3	15.1	67.1	10.1
X	5517-09	3	14.2	81.8	11.6
XI	5473-01	3	23.3	6.5	1.5
XII	5504-19	3	13.0	52.6	6.8

Example XIII

Magnesium chloride was dissolved in water and hydrolyzed with aqueous sodium hydroxide. The magnesium hydroxide precipitate that formed was collected by filtration, washed with water, dried at 110°C. and then calcined at 500°C. in air for 16 hours. This calcined magnesium hydroxide support was impregnated with aqueous sodium permanganate to a 13 percent loading of the permanganate and then calcined at 1000°C. in air for 16 hours. The contact agent composition contained 5 weight percent manganese and 2.1 weight percent sodium on magnesia. The contact agent was run in the methane conversion process to yield the results shown in Table 3 below.

Table 3

°C	GHSV hr^{-1}	% Conv	Selectivity C_2+	C_2	C_3	C_{4-7}	CO	CO_2	Coke
825	1200	23.8	33.1	15.0	5.8	4.3	1.5	40.2	0
850	1200	28.2	28.4	12.6	4.9	3.5	4.3	46.2	0
825	600	42.5	26.6	9.2	4.7	14.9	0	44.4	0

Example XIV

Magnesium chloride was dissolved in water and hydrolyzed with aqueous sodium hydroxide. The magnesium hydroxide precipitate that formed was collected by filtration, washed with water and dried at 110°C. This dried magnesium hydroxide cake was impregnated with aqueous sodium permanganate to a 13 percent loading of the permanganate and calcined at 1000°C. in air for 16 hours. The contact agent composition contained 5 weight percent manganese and 2.1 weight percent sodium on magnesia. The contact agent was run in the methane conversion process to yield the results shown in Table 4 below.

Table 4

°C	GHSV hr^{-1}	% Conv	Selectivity C_2+	C_2	C_3	C_{4-7}	CO	CO_2	Coke
825	1200	23.1	11.5	12.7	1.7	.7	0	70.4	2.9
825	600	36.5	14.1	10.0	2.2	.7	0	72.9	6.6

Example XV

The procedure of Example XIII was repeated, except that magnesium acetate was substituted for magnesium chloride. The results of the methane runs are shown in Table 5 below.

Table 5

°C	GHSV hr^{-1}	% Conv	Selectivity C_2+	C_2	C_3	C_{4-7}	CO	CO_2	Coke
825	1200	10.5	38.0	38.0	5.7	3.8	0	13.6	.8
850	1200	11.6	34.4	28.0	5.2	2.9	0	27.9	1.6
825	600	16.7	43.5	34.0	6.3	4.2	0	11.4	.6

Example XVI

Magnesium acetate was calcined at 450°C. in air for 16 hours to yield magnesium oxide. This calcined magnesium oxide was impregnated with aqueous sodium permanganate to a 13 percent loading of the permanganate and calcined at 1000°C. in air for 16 hours. The contact agent composition contained 5 weight percent manganese and 2.1 weight percent sodium on magnesia. The contact agent was run in the methane conversion process to yield the results shown in Table 6 below.

Table 6

Temp °C	GHSV, hr^{-1}	% Conversion	% C_2 Selectivity
800	600	32.5	27.5
825	600	36.0	21.0
825	1200	22.0	18.0

WHAT IS CLAIMED IS:

1. A catalyst composition comprising:

(a) at least one metal, the oxide of which is reducible upon contact with methane at selected temperatures in the range of about 500° to 1000°C. to produce higher hydrocarbons and water;

(b) at least one alkali metal; and

(c) a support comprising at least one member of a group consisting of oxides of silicon, oxides of alkaline earth metals, and mixed oxides of silicon and at least one alkaline earth metal.

2. The composition of claim 1 wherein said at least one metal is selected from the group consisting of manganese, tin, indium, germanium, antimony, lead, bismuth, and mixtures thereof.

3. The composition of claim 1 wherein said alkaline earth metal is selected from a group consisting of lithium, sodium, potassium, rubidium, cesium, and mixtures thereof.

4. The composition of claim 3 wherein said alkali metal is selected from a group consisting of sodium, sodium compounds, and mixtures thereof.

5. The composition of claim 1 wherein said support comprises at least two oxides.

6. The composition of claim 5 wherein said support comprises magnesia.

7. The composition of claim 5 wherein said support comprises silica.

8. The composition of claim 7 wherein said support comprises magnesia and silica.

9. The composition of claim 8 wherein said support comprises a mole ratio of said first oxide to said silica of about 50:1 to about 1:1.

10. The composition of claim 9 wherein said magnesia to said silica in said support comprises a ratio of about 30:1 to about 5:1.

11. The composition of claim 10 wherein said mole ratio of said silica to said alkali metal comprises a ratio of about 0.5:1 to about 10:1.

12. The composition of claim 9 wherein said support is produced by the steps comprising combining hydroxylated magnesia with a component of silicon which forms silica and is readily suspendable in a continuous medium.

13. The composition of claim 12 wherein said silicon component is suspended as a gel or a solution.

14. The composition of claim 12 wherein said silicon component is selected from a group consisting of colloidal silica, sodium silicate, and mixtures thereof.

15. The composition of claim 14 wherein said silicon component comprises about 5 to about 15 weight percent of said composition.

16. The composition of claim 15 wherein said silicon component comprises about 10 weight percent of said composition.

17. The composition of claim 1 wherein the surface of at least a portion of said support is sintered at an elevated temperature prior to the addition of said at least one metal.

18. The composition of claim 17 wherein said sintering comprises heating said support to about 0.33 of the normal melting temperature of the material of said support.

19. The composition of claim 17 wherein said support comprises magnesia and is sintered at a temperature of about 1690° to about 5070°F.

20. The composition of claim 17 wherein said support comprises silica and is sintered at a temperature of about 1040° to about 3110°F.

21. The composition of claim 17 wherein the surface area of said support ranges from about 30 to about 90 square meters per gram.

22. The composition of claim 6 wherein said support comprises hydroxylated magnesia.

23. The composition of claim 22 wherein said hydroxylated magnesia is derived from magnesium hydroxide.

24. The composition of claim 22 wherein said hydroxylated magnesia comprises a magnesium-containing component contacted with a hydroxyl-containing material.

25. The composition of claim 1 wherein said support is calcined prior to the addition of said at least one metal.

26. The composition of claim 1 wherein said at least one metal comprises manganese and wherein the amount of said manganese present is within the range of about 1 to about 40 weight percent based upon the combined weight of said manganese and said support, said composition being substantially free of catalytically effective iron.

27. The composition of claim 26 wherein the atomic ratio of said alkali metal to said manganese is within the range of about 0.01:1 to about 10:1.

28. The composition of claim 27 wherein the amount of said manganese is within the range of about 5 to about 30 weight percent based upon the combined weight of said manganese and said support.

29. The composition of claim 26 wherein said composition satisfies the formula:

$$MnA_aSi_bO_x$$

wherein A is at least one alkali metal, a is within the range of about 0.01 to 10, b is within the range of about

0.5 to 90, and x is the number of oxygen atoms required by the valence states of the other elements.

30. The composition of claim 29 wherein A is sodium.

31. The composition of claim 30 wherein a is within the range of about 0.1 to about 3.3.

32. The composition of claim 29 wherein A is lithium.

33. The composition of claim 29 wherein A is potassium.

34. The composition of claim 29 wherein b is within the range of about 0.9 to about 17.4.

35. The composition of claim 29 wherein b is within the range of about 2 to about 15.

36. The composition of claim 26 wherein said composition satisfies the formula:

$$MnA_aMg_bO_x$$

wherein A is at least one alkali metal, a is within the range of about 0.01 to about 10, b is within the range of about 3 to about 80, and x is the number of oxygen atoms required by the valence states of the other elements.

37. The composition of claim 36 wherein A is sodium.

38. The composition of claim 37 wherein a is within the range of about 0.1 to about 3.3.

39. The composition of claim 36 wherein A is lithium.

40. The composition of claim 36 wherein A is potassium.

41. The composition of claim 36 wherein b is within the range of about 5 to about 12.

42. The composition of claim 26 wherein said composition satisfies the formula:

$$MnA_aB_bO_x$$

wherein A is at least one alkali metal, B is at least one member of the group consisting of calcium, strontium, and barium a is within the range of about 0.01 to about 10, b is within the range of about 0.1 to about 100, and x is the number of oxygen atoms required by the valence states of the other elements.

43. The composition of claim 42 wherein B is calcium.

44. The composition of claim 42 wherein A is sodium.

45. The composition of claim 44 wherein a is within the range of about 0.1 to about 3.3.

46. The composition of claim 42 wherein A is lithium.

47. The composition of claim 42 wherein A is potassium.

48. The composition of claim 42 wherein b is within the range of about 1 to about 7.

49. The composition of claim 26 wherein said composition satisfies the formula:

$$MnA_aCa_bO_x$$

wherein A is at least one alkali metal, a is within the range of about 0.01 to about 10, b is within the range of about 0.4 to about 100, and x is the number of oxygen atoms required by the valence states of the other elements.

50. The composition of claim 49 wherein A is sodium.

51. The composition of claim 50 wherein a is within the range of about 0.1 to about 3.3.

52. The composition of claim 49 wherein A is lithium.

53. The composition of claim 49 wherein A is potassium.

54. The composition of claim 49 wherein b is within the range of about 4 to 20.

55. The composition of claim 26 wherein said composition satisfies the formula:

$$MnA_aB_bSi_cO_x$$

wherein A is at least one alkali metal, B is at least one alkaline earth metal, a is within the range of about 0.01 to about 10, b is within the range of about 0.1 to about 90, c is within the range of about 1 to about 90, the sum of b plus c is greater than about 1, and x is the number of oxygen atoms required by the valence states of the other elements.

56. The composition of claim 55 wherein B is magnesium.

57. The composition of claim 56 wherein b is within the range of about 0.6 to about 10.

58. The composition of claim 56 wherein the ratio c to b is within the range of about 2:1 to about 3:1.

59. The composition of claim 56 wherein the ratio b to c is within the range of about 5:1 to about 30:1.

60. The composition of claim 55 wherein B is calcium.

61. The composition of claim 60 wherein b is within the range of about 0.4 to about 10.

62. The composition of claim 55 wherein B is barium.

63. The composition of claim 62 wherein b is within the range of about 0.1 to about 5.

64. The composition of claim 55 wherein A is sodium.

65. The composition of claim 64 wherein a is within the range of about 0.1 to about 3.3.

66. The composition of claim 55 wherein A is lithium.

67. The composition of claim 55 wherein A is potassium.

68. A method for conversion of a gas comprising methane which comprises contacting said gas with a contact agent at conditions to convert said gas, said contact agent comprising:

(a) at least one metal, the oxide of which is reduced and produces higher hydrocarbons upon contact with methane at selected temperatures within the range of about 500° to about 1000°C.;

(b) an alkali metal; and

(c) a support comprising at least one member of a group consisting of oxides of silicon, oxides of alkaline earth metals, and mixed oxides of silicon and at least one alkaline earth metal.

69. The method of claim 68 wherein said at least one metal is selected from a group consisting of manganese, tin, indium, germanium, antimony, lead, bismuth, and mixtures thereof.

70. The method of claim 68 wherein said alkaline earth metal is selected from a group consisting of lithium, sodium, potassium, rubidium, cesium, and mixtures thereof.

71. The method of claim 70 wherein said alkali metal is selected from a group consisting of sodium, sodium compounds, and mixtures thereof.

72. The method of claim 68 wherein said support comprises at least two oxides.

73. The method of claim 72 wherein said support comprises magnesia.

74. The method of claim 73 wherein said support comprises silica.

75. The method of claim 74 wherein said support comprises magnesia and silica.

76. The method of claim 74 wherein said support comprises a mole ratio of said first oxide to said silica of about 50:1 to about 1:1.

77. The method of claim 76 wherein said magnesia to said silica in said support comprises a ratio of about 30:1 to about 5:1.

78. The method of claim 77 wherein said mole ratio of said silica to said alkali metal comprises a ratio of about 0.5:1 to about 10:1.

79. The method of claim 75 wherein said support is produced by the steps comprising combining hydroxylated magnesia with a component of silicon which forms silica and is readily suspendable in a continuous medium.

80. The method of claim 79 wherein said silicon component is suspended as a gel or a solution.

81. The method of claim 79 wherein said silicon component is selected from the group consisting of colloidal silica, sodium silicate, and mixtures thereof.

82. The method of claim 81 wherein said silicon component comprises about 5 to about 15 weight percent of said composition.

83. The method of claim 82 wherein said silicon component comprises about 10 weight percent of said composition.

84. The method of claim 68 wherein the surface of at least a portion of said support is sintered at an elevated temperature prior to said contacting.

85. The method of claim 84 wherein said sintering comprises heating said support to about 0.33 of the normal melting temperature of the material of said support.

86. The method of claim 84 wherein said support comprises magnesia and is sintered at a temperature of about 1690° to about 5070°F.

87. The method of claim 84 wherein said support comprises silica and is sintered at a temperature of about 1040° to about 3110°F.

88. The method of claim 84 wherein the surface area of said support ranges from about 30 to about 90 square meters per gram.

89. The method of claim 73 wherein said support comprises hydroxylated magnesia.

90. The method of claim 89 wherein said hydroxylated magnesia is derived from magnesium hydroxide.

91. The method of claim 89 wherein said hydroxylated magnesia comprises a magnesium-containing component contacted with hydroxyl-containing material.

92. The method of claim 68 wherein said support is calcined prior to the addition of said at least one metal.

93. The method of claim 68 wherein said at least one metal comprises manganese and wherein the amount of said manganese present is within the range of about 1 to about 40 weight percent based upon the combined weight of said manganese and said support, said composition being substantially free of catalytically effective iron.

94. The method of claim 93 wherein the atomic ratio of said alkali metal to said manganese is within the range of about 0.01:1 to about 10:1.

95. The method of claim 94 wherein the amount of said manganese is within the range of about 5 to about 30 weight percent based upon the combined weight of said manganese and said support.

96. The method of claim 93 wherein said composition satisfies the formula:

$$MnA_aSi_bO_x$$

wherein A is at least one alkali metal, a is within the range of about 0.01 to about 10, b is within the range of about 0.5 to about 90, and x is the number of oxygen atoms required by the valence states of the other elements, said composition being substantially free of catalytically effective iron.

97. The method of claim 96 wherein A is sodium.

98. The method of claim 97 wherein a is within the range of about 0.1 to about 3.3.

99. The method of claim 96 wherein A is lithium.

100. The method of claim 96 wherein A is potassium.

101. The method of claim 96 wherein b is within the range of about 0.9 to about 17.4.

102. The method of claim 96 wherein b is within the range of about 2 to about 15.

103. The method of claim 93 comprising manganese-containing oxides, at least one alkali metal or compound thereof, and at least one oxide of manganese, said composition satisfying the formula:

$$MnA_aMg_bO_x$$

wherein A is at least one alkali metal, a is within the range of about 0.01 to about 10, b is within the range of about 3 to about 80, and x is the number of oxygen atoms required by the valence states of the other elements.

104. The method of claim 103 wherein A is sodium.

105. The method of claim 104 wherein a is within the range of about 0.1 to about 3.3.

106. The method of claim 103 wherein A is lithium.

107. The method of claim 103 wherein A is potassium.

108. The method of claim 103 wherein b is within the range of about 5 to about 12.

109. The method of claim 93 comprising manganese-containing oxides, at least one alkali metal or compound thereof, and at least one member of a group consisting of oxides of calcium, strontium, and barium, said composition satisfying the formula:

$$MnA_aB_bO_x$$

wherein A is at least one alkali metal, B is at least one member of a group consisting of calcium, strontium, and barium, a is within the range of about 0.01 to about 10, b is within the range of about 0.1 to about 100, and x is the number of oxygen atoms required by the valence states of the other elements.

110. The method of claim 109 wherein B is calcium.

111. The method of claim 109 wherein A is sodium.

112. The method of claim 111 wherein a is within the range of about 0.1 to about 3.3.

113. The method of claim 109 wherein A is lithium.

114. The method of claim 109 wherein A is potassium.

115. The method of claim 109 wherein b is within the range of about 1 to about 7.

116. The method of claim 93 comprising manganese-containing oxides, at least one alkali metal or compound thereof, and CaO, said composition satisfying the formula:

$$MnA_aCa_bO_x$$

wherein A is at least one alkali metal, a is within the range of about 0.01 to about 10, b is within the range of about 0.4 to about 100, and x is the number of oxygen atoms required by the valence states of the other elements.

117. The method of claim 116 wherein A is sodium.

118. The method of claim 117 wherein a is within the range of about 0.1 to about 3.3.

119. The method of claim 116 wherein A is lithium.

120. The method of claim 116 wherein A is potassium.

121. The method of claim 116 wherein b is within the range of about 4 to about 20.

122. The method of claim 93 comprising manganese-containing oxides, at least one alkali metal or compound thereof, and mixed oxides of silicon and at least one alkaline earth metal, said composition satisfying the formula:

$$MnA_aB_bSi_cO_x$$

wherein A is at least one alkali metal, B is at least one alkaline earth metal, a is within the range of about 0.01 to about 10, b is within the range of about 0.1 to about 90, c is within the range of about 1 to about 90, the sum of b plus c is greater than about 1, and x is the number of oxygen atoms required by the valence states of the other elements.

123. The method of claim 122 wherein B is magnesium.

124. The method of claim 123 wherein b is within the range of about 0.6 to about 10.

125. The method of claim 123 wherein the ratio b:c is within the range of about 2:1 to about 3:1.

126. The method of claim 123 wherein the ratio b:c is within the range of about 5:1 to about 30:1.

127. The method of claim 122 wherein B is calcium.

128. The method of claim 127 wherein b is within the range of about 0.4 to about 10.

129. The method of claim 122 wherein B is barium.

130. The method of claim 129 wherein b is within the range of about 0.1 to about 5.

131. The method of claim 122 wherein A is sodium.

132. The method of claim 131 wherein a is within the range of about 0.1 to about 3.3.

133. The method of claim 122 wherein A is lithium.

134. The method of claim 122 wherein A is potassium.

INTERNATIONAL SEARCH REPORT

International Application No PCT/US85/00687

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [3]

According to International Patent Classification (IPC) or to both National Classification and IPC

INT. CL. 3 B01J 21/00, B01J 23/04, C07C 2/00
U.S. CL. 502/241, 242, 243, 249, 324, 340, 585/500

II. FIELDS SEARCHED

Minimum Documentation Searched [4]

Classification System	Classification Symbols
U.S.	502/241, 242, 243, 249, 325, 340 585/415, 417, 418, 500, 541, 654, 656, 658, 661, 700, 741, 943

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [5]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [14]

Category *	Citation of Document, [16] with indication, where appropriate, of the relevant passages [17]	Relevant to Claim No. [18]
Y	US, A, 3,804,902, (Sakakibara et al) 16 April 1974	1-4,7,26-35
A	US, A, 3,838,069, (Miyazaki et al) 24 September 1974	1-67
A	US, A, 4,397,771, (Grasselli et al) 09 August 1983	1-67
Y	US, A, 3,494,972, (Friedli), 10 February 1970	1-4,7,26-35
A	US, A, 3,668,148, (Van Beek et al) 06 June 1972	1-67
Y	US, A, 3,987,104, (Vanhauten) 19 October 1976	1-4, 7
Y	US, A, 4,021,371, (Petro et al) 03 May 1977	1-67
Y	US, A, 3,928,238, (Koberstein et al) 23 December 1972	1-67
Y	US, A, 3,642,930, (Graselli et al) 15 February 1972	1-4

* Special categories of cited documents: [15]

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search [2] 28 June 1985	Date of Mailing of this International Search Report [2] 11 JUL 1985
International Searching Authority [1] ISA/US	Signature of Authorized Officer [20] Cynthia A. Prezlock Cynthia A. Prezlock

International Application No. PCT/US85/00687

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category *	Citation of Document, [16] with indication, where appropriate, of the relevant passages [17]	Relevant to Claim No [18]
A	US, A, 4,205,194, (Mitchell, III et al) 27 May 1980	68-134
A	US, A, 4,239,658, (Mitchell, III et al) 16 December 1980	68-134

FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

A,P	US, A, 4,443,645, (Jones et al), 17 April 1984	68-134
A,P	US, A, 4,443,648, (Jones et al), 17 April 1984	68-134
A	N, Journal of Catalysis, issued 1982, G.E. Keller and M.M. Bhasin, Synthesis of Ethylene via Oxidative Coupling of Methane, See pages 9-18	
A	N, Journal of the Chinese Chemical Society, Trelant Fang and Chuin-Teh Yeh, Catalytic Pyrolysis of Methane, See pages 265-273	68-134

V.☐ **OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE** [10]

This international search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:

1.☐ Claim numbers ...., because they relate to subject matter [12] not required to be searched by this Authority, namely:

2.☐ Claim numbers ...., because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out [13], specifically:

VI.☐ **OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING** [11]

This International Searching Authority found multiple inventions in this international application as follows:

1.☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.

2.☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:

3.☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:

4.☐ As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority did not invite payment of any additional fee.

Remark on Protest

☐ The additional search fees were accompanied by applicant's protest.

☐ No protest accompanied the payment of additional search fees.